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# New Materials for Organic Electronics: Improved Properties to Tackle Application Challenges

Mario Caironi,\* Christian Müller, Elizabeth von Hauff, and Michael Sommer

From the 22<sup>nd</sup> to the 26<sup>th</sup> of May 2017, Strasbourg hosted the annual Spring Meeting of the European Materials Research Society (E-MRS), an important gathering in the calendar of materials scientists from around the world. Symposium L was dedicated to “New materials for organic electronics: from synthesis to processing, characterization and device physics”. The Symposium comprised 21 invited speakers from 9 different countries and attracted more than 120 oral and poster contributions on the latest advancements in organic conjugated small molecules and polymers, as well as their use in combination with hybrid materials, for electronic and energy applications. Various topics were covered, from synthesis of novel materials, to processing schemes and additives such as dopants and binders, to insights into structure-processing-property relationships, all the way to opto- and micro-electronic devices with enhanced performances and improved electronic and mechanical stability. The result was an open discussion of key aspects towards the widespread application of organic electronics, and on the understanding of how molecular design, nanostructure and device performance are intimately linked.

This Special Issue summarizes some of the advances presented at symposium L and contains invited contributions from leaders in the field. While most of the potential advantages of organic electronics were postulated decades ago, organic light emitting diodes are the only organic electronic application to have successfully entered the market. However, after over thirty years of intense research, we are now beginning to see innovations in organic electronics that are approaching commercialization. Organic semiconductors offer infinite possibilities to create new materials with tailored optical and electrical properties. Every day new materials are being added to

the existing plethora of organic semiconductors. Their application in devices such as solar cells, thin-film transistors, sensors and thermoelectric generators continuously adds to our understanding of relevant structure-property relationships. This insight then provides critical feedback for the design of the next generation of organic semiconductors, with beneficial consequences on the performances and wider potential for real life applications. Despite this progress, great challenges still have to be faced and works collected in this Special Issue are an interesting window on how such challenges are being tackled and solved towards next-generation organic electronics.

Solved from the synthetic point of view, H. Usta and co-workers present physicochemical and optoelectronic properties of a new low band-gap, *meso*-substituted BODIPY co-polymer, which achieved a record high power conversion efficiency in bulk heterojunction solar cells for boron-containing donor polymers. Further, M. Heeney and co-workers investigate the backbone fluorination of polythiophenes in order to achieve control over the dielectric constant of organic films, which should allow more efficient power conversion efficiency. The self-assembling properties of new oligothiophene derivatives are exploited by P. Samori and co-workers towards the development of fast and high sensitive water sensors. Miscibility of polymers with molecular dopants is studied by M. Sommer and co-workers, who propose the introduction of covalently incorporated, kinked monomers into co-polymers characterized otherwise by a straight backbone, as a method to increase doping efficiency. Indeed, electronic doping is gaining renewed interest in the community, both for thermoelectric applications, with the promise of future lightweight and cheap organic thermoelectric generators, and in general for optimized electronic devices. For example, T. Anthopoulos and co-workers highlight the role of molecular p-doping in high-mobility small-molecule/polymer blend transistors, achieving at the same time an improvement in charge mobility and device stability, and a reduction in contact resistance.

Besides an extensive search for new and higher performing materials, it is essential to understand the underlying structure-property relationships by gaining insights into the electronic and mechanical properties of organic films for use in flexible electronics applications. W. Maes and collaborators, in an interesting Progress Report, elucidate the real nature of broadly applied donor-acceptor “push-pull” co-polymers: the nominal alternating structure easily sees the presence of homo-couplings, locally altering the electronic properties along the backbone, as well as unexpected chain ending groups. H. Sirringhaus and co-workers investigate a critical aspect for charge transport in semiconducting polymers, the correlation among disorder and molecular structure in a series of indacenodithiophene-based semiconducting polymer derivatives.

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Such studies are contributing to rationalize molecular design to achieve even more efficient polymer semiconductors, which albeit presenting large area uniformity, still suffer from limited performance as compared to small molecules especially in field-effect transistors. At the same level, linking molecular structure to mechanical and conductive properties is crucial for compliant flexible electronics, a topic which is addressed in the Progress Report by E. Gomez et al.

Insights into how molecular structure and packing favor transport allow to devise advanced processing techniques. Uniaxial alignment of polymer semiconductors in this sense has been recently shown to lead to improved field-effect mobility along the backbone direction. M. Brinkmann and co-workers here achieve oriented films of the polymer semiconductor PTB7 by high-temperature rubbing and isothermal crystallization, giving rise to a high dichroic ratio and anisotropic hole mobility. M. Mas-Torrent and co-workers apply instead a large-area coating, known as bar-assisted meniscus shearing, to deposit small molecule thin films for high performance electrolyte gated transistors.

The Special Issue sees a relevant number of contributions dedicated to many aspects of organic solar cells, which recently are being commercially installed for outdoor large-area applications and are developed for interesting indoor applications enabling domotics and the Internet of Things. Fundamental losses in these devices are reviewed by C. Deibel and co-workers, offering both kinetic and energetic viewpoints on non-geminate, non-radiative charge recombination. The fundamental role of additives in the formation of the fine bulk-heterojunction microstructure are addressed in two different works: D. Baran and co-workers explore the opposite effect on performance of additives in blends based on fullerene and non-fullerene acceptors, while C. K. Luscombe and co-workers show how low-boiling point additives can achieve at the same time high performance and improved oxidative stability, a critical aspect for improving the lifetime of organic photovoltaics installations. Additives are just one of the ingredients that has to be tuned to achieve optimal power conversion efficiency, and this optimization process requires tuning of the device within a multi-dimensional space, where blend composition, temperature, primary solvents, represent interdependent knobs, thus requiring an extensive amount of time, besides materials usage, in order to pursue a satisfactory evaluation. To overcome this bottleneck M. Campoy-Quiles and co-workers propose a multi-parametric approach based on the adoption of thickness, compositional and nanostructural gradients within the same large-area blade-coated film in order to drastically shorten the screening of the photovoltaic material potential. Large-area processing of multilayer organic stacks has a profound effect on the efficiency of fabrication technologies. To this end, a contribution by M. Caironi and co-workers proposes the adoption of a simple and scalable tattoo-paper based technique for the gentle lamination of hole-transporting interlayers on top of organic absorbers in order to simplify this typically critical step, especially towards the manufacturing of very cheap indoor organic photovoltaic modules. Interestingly, organic semiconductors are also critically important in the development of highly efficient and stable new generation hybrid perovskite solar cells, as in the case of fullerene derivatives, a topic reviewed by F. Gao and co-workers. Photon to electron conversion in organics can also



**Mario Caironi** obtained his Ph.D. in 2007 at Politecnico di Milan (Italy), with a thesis on organic photodetectors and memory devices. In the same year, he joined Prof. Sirringhaus' group at Cambridge (UK) as a postdoc, to work on printed, down-scaled polymer transistors and circuits. In 2010 he was appointed as a Team Leader

at Istituto Italiano di Tecnologia (Milan, Italy), where he leads the Printed and Molecular Electronics group from 2014, when he received an ERC Starting Grant. He is currently interested in high resolution printing techniques for opto-electronic and thermoelectric devices fabrication, in the device physics of organic transistors and their integration in high-frequency printed circuits, and biomedical and healthcare devices.



**Christian Müller** is a Professor in Polymer Science at Chalmers. He received an ERC Starting Grant in 2014 and is a Wallenberg Academy Fellow. In 2016, he became a SSF Future Research Leader. Prior to Chalmers, where he has worked since 2012, he completed postdoctoral stays at ICMAB-CSIC in Barcelona and Linköping University.

He holds a Dr.Sc. in Materials Science from ETH Zürich (2008) and a M.Sci. in Natural Sciences from Cambridge University (2004). His research interests include the use of organic semiconductors, polymer blends, and composites for energy technologies ranging from solar cells and thermoelectrics to power cables.



**Elizabeth von Hauff** studied Physics at the University of Alberta in Edmonton, Canada. Her Ph.D. work was at the University of Oldenburg, Germany, with a focus on charge carrier transport in organic semiconductors. In 2011, Elizabeth completed her habilitation in experimental physics, and then accepted a joint appointment as

Associate Professor between the Institute of Physics at the University of Freiburg and the Fraunhofer Institute for Solar Energy Systems (ISE). In 2013, Elizabeth was appointed Associate Professor in Physics at the VU Amsterdam. She is interested in fundamental questions in physics and chemistry within the context of real applications.



**Michael Sommer** obtained his Ph.D. in 2009 on semi-conducting block copolymers for organic electronic devices under the supervision of Mukundan Thelakkat at the University of Bayreuth, Germany. In 2010, he joined the group of Wilhelm Huck at the Department of Chemistry, University of Cambridge, UK, as a post-doctoral researcher.

From 2012, he was group leader at the Department of Macromolecular Chemistry the Albert-Ludwigs-University of Freiburg, Germany. He is full professor for Polymer Chemistry at TU Chemnitz, Germany, since 2017. His research interests encompass the synthesis of conjugated materials, controlled polymerization methods, self-assembly and structure–function relationships of electronically active materials.

be advantageously exploited in efficient light detectors: in their work dedicated to organic photo-diodes, G. Hernandez-Sosa and co-workers show the improvement of detection speed by blending absorbers with insulating polymers while conserving steady state performance.

An important building block in opto-electronics devices is without doubt represented by transparent electrodes. Processability, flexibility, and potential for integration in devices, of various classes of transparent electrodes are reviewed by G. Hadzioannou and co-workers, while J. Zaumseil and co-workers address injection in carbon based field-effect transistors from dense networks of carbon nanotubes, achieving improved injection into polymer semiconductors.

As it is evident from the contributions in this special issue and from the recent literature, organics are witnessing a spectacular increase in performance, allowing, for example, the targeting of solar cells in the lab with quantum efficiencies above 15% and transistors with charge mobility well above  $10 \text{ cm}^2 \text{ Vs}^{-1}$ . Such achievements will contribute to the reinforcement of opportunities for achieving marketable products, on top of the first niche applications. Yet, to favor this process, scientists and engineers will have to handle such figure of merits with care, discussing and agreeing on solid terms under which to report them, and adopting the most suitable ones for each application. For example, in his interesting Progress Report “Will We See Gigahertz Organic Transistors?”, H. Klauk warns us against the mobility hype, which is not free from questionable extraction procedures and therefore questionable record values, and clearly underlines how, in order to improve the speed of downscaled organic transistors, the key parameter is contact resistance. Organics are also being further explored for other very appealing purposes, such as wearable and ultra-conformable healthcare devices, where bioelectronics and biosensors may have a huge impact for point-of-care applications. Energy requirements of such distributed devices may be satisfied in the future by wearable photovoltaics, as well as cheap and economically viable thermoelectrics, a topic which is seeing a re-burst of interest in the field. The same horizon depicted in the Review by Klauk can lead us to a new frontier of flexible, large-area radio-frequency electronics, which have the potential to vastly extend the applicability of organics, letting us foresee wireless applications that utilize local area networks without the need of silicon chips. Whether such optimistic estimations will find their way into our daily lives will be determined by several factors, some of which fall outside scientific evidence and technological development. Yet, the nominally infinite possibility of devising new molecular structures, and the advances in knowledge regarding structure-property relationships, are likely to bring us even more competitive organic electronic materials.